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THE DISSOCIATION ENERGY OF GASEOUS TITANIUM MONONITRIDE

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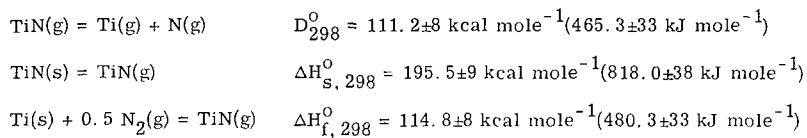
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ABSTRACT

The titanium nitride (TiN) molecule has been identified in the vapor phase over solid $TiN_{0.78}$ at temperatures above 2250 K. The Knudsen effusion method was used in conjunction with a double-focusing mass spectrometer. The high resolution of the spectrometer made possible the identification of the TiN molecule. From experimentally determined partial pressures, the enthalpy for the reaction $TiN(g) = Ti(g) + 0.5 N_2(g)$ has been calculated as $\Delta H^O_{298} = -1.8 \pm 7$ kcal mole^{-1} (-7.5 ± 29 kJ mole^{-1}). This reaction enthalpy yields thermodynamic properties for gaseous TiN when combined with published thermodynamic data:

$TiN(g) = Ti(g) + N(g)$ $\qquad D^O_{298} = 111.2 \pm 8$ kcal mole^{-1}(465.3 ± 33 kJ mole^{-1})

$TiN(s) = TiN(g)$ $\qquad \Delta H^O_{s, 298} = 195.5 \pm 9$ kcal mole^{-1}(818.0 ± 38 kJ mole^{-1})

$Ti(s) + 0.5 N_2(g) = TiN(g)$ $\qquad \Delta H^O_{f, 298} = 114.8 \pm 8$ kcal mole^{-1}(480.3 ± 33 kJ mole^{-1})

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SUMMARY

The titanium nitride (TiN) molecule has been identified in the vapor phase over solid $TiN_{0.78}$ at temperatures above 2250 K. The Knudsen effusion method was used in conjunction with a double-focusing mass spectrometer. The high resolution of the spectrometer made possible the identification of the TiN molecule. From experimentally determined partial pressures, the enthalpy for the reaction $TiN(g) = Ti(g) + 0.5 N_2(g)$ has been calculated as $\Delta H^O_{298} = -1.8 \pm 7$ kilocalories mole^{-1} (-7.5 ± 29 kJ mole^{-1}). This reaction enthalpy yields the following thermodynamic properties for gaseous TiN when combined with published thermodynamic data:

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Our experimental value of D^O_{298} is compared with estimated values of approximately 125 kilocalories mole^{-1} (523 kJ mole^{-1}).

INTRODUCTION

The high-temperature vaporization of the solid titanium nitride (TiN) phase of various stoichiometries has been the subject of several recent investigations. Akishin and Klodeev (ref. 1) attempted to detect directly by mass spectrometric analysis gaseous TiN in the equilibrium vapor above TiN_x. They failed to identify TiN; however, they reported a value of 2×10^{-8} atmosphere (2×10^{-3} N/m^2) at 2073 K as the upper limit for

the pressure of gaseous TiN. Hock, et al., (ref. 2) concluded from their Knudsen effusion experiments with $TiN_{0.8}$ that the only significant gaseous species in equilibrium with the solid were Ti and N_2. They reported the heat of decomposition of solid TiN, according to the reaction $TiN(s) = Ti(g) + 0.5 N_2(g)$ as $\Delta H_0^O = 191.20 \pm 0.96$ kilocalories $mole^{-1}$ $(800.0 \pm 4.0$ kJ $mole^{-1})$. They also presented equations for the partial pressures of Ti and N_2 as a function of temperature over the range 1987 to 2241 K. Parkinson and Reeves used shock excited optical spectroscopy and have attributed a series of bands near 3100 Å to gaseous TiN (ref. 3).

The dissociation energy D_0^O of diatomic TiN has been estimated by Carlson, et al., (ref. 4) on the basis of ab initio calculations on TiN and a comparison of the calculated and experimental values of the isoelectronic scandium oxide (ScO) molecule. The value obtained was $D_0^O = 125$ kilocalories $mole^{-1}$ (523 kJ $mole^{-1}$). While this is a reasonable number, it should be considered only a crude estimate because the uncertainty associated with it must be relatively large. On the other hand, Gingerich (ref. 5) used the empirical α-parameter method of Colin and Goldfinger (ref. 6) to predict a value of D_{298}^O $= 123 \pm 10$ kilocalories $mole^{-1}$ $(515 \pm 42$ kJ $mole^{-1})$ for TiN. The value of α used was based on his experimentally determined dissociation energies and heats of atomization of zirconium nitride (ZrN), thorium nitride (ThN), and uranium nitride (UN).

We have estimated that gaseous TiN should be detectable by refined molecular beam mass spectrometric methods at temperatures above 2200 K. This estimate was based on the predicted dissociation energy of 125 kilocalories $mole^{-1}$ (523 kJ $mole^{-1}$) and measured partial pressures for Ti and N_2. The purpose of this investigation was first to detect the gaseous TiN molecule and then to measure its equilibrium partial pressure together with the partial pressures of its component elements, and finally to derive from these measurements thermodynamic data.

MASS SPECTROMETER

In this investigation we used a modified Consolidated Electrodynamics Corp. model 21-110 mass spectrometer equipped with a Knudsen cell assembly designed and built at Lewis Research Center. The mass spectrometer is double focusing and of the Mattauch-Herzog type. A schematic diagram of the entire apparatus is shown in figure 1, and schematic cross-section diagrams of the Knudsen cell assembly and ion source are shown in figure 2. Actual views of the Knudsen cell assembly are shown in figures 3 and 4.
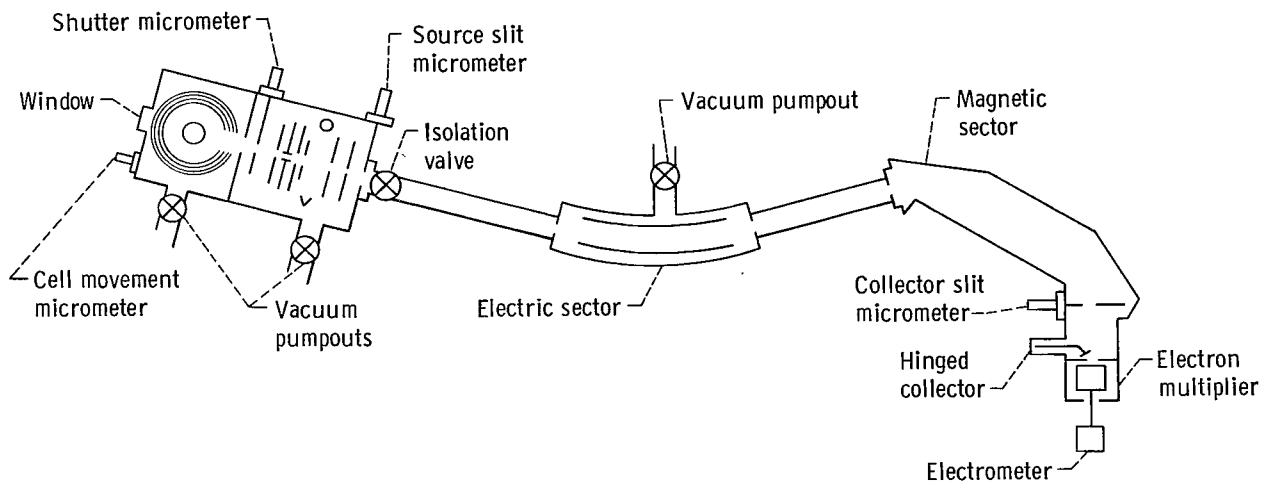
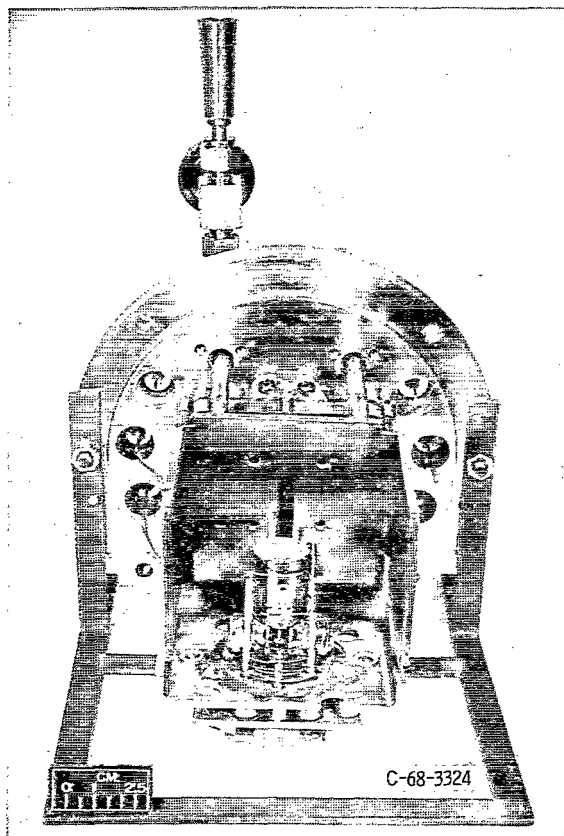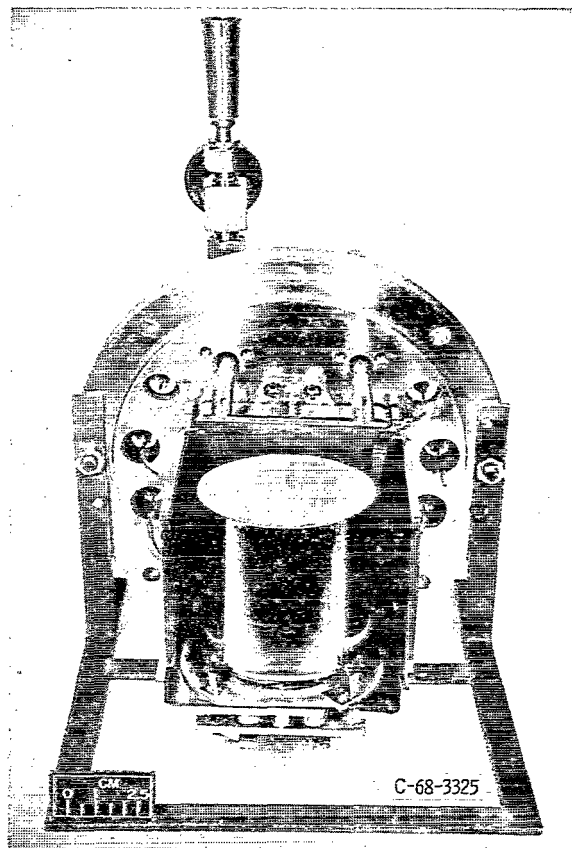Figure 1. - Schematic of mass spectrometer and Knudsen cell inlet system.
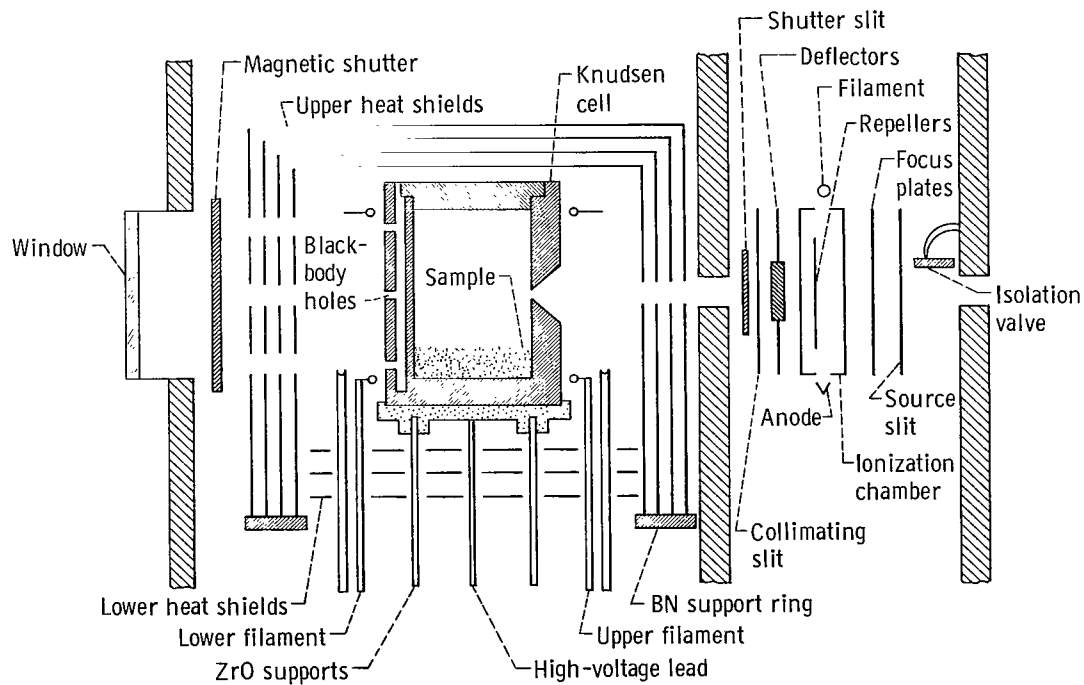
Figure 2. - Schematic of Knudsen cell assembly and ion source.

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(a) Without heat shields.   (b) With heat shields in place.
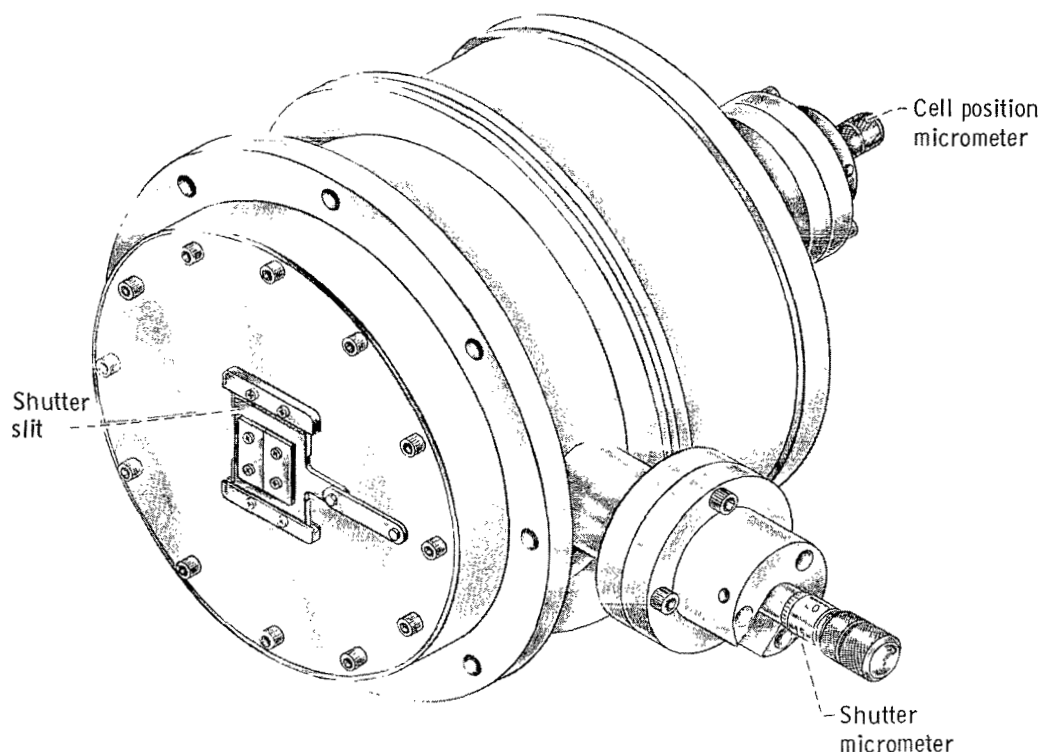
Figure 3. – Knudsen cell assembly.

Figure 4. - Knudsen cell housing.

Knudsen Cell Assembly

The Knudsen cell assembly used in this study is uncommon in that the effusion orifice is in the curved side of the cylindrical Knudsen cell. This design, which produced an ion beam coaxial with the molecular beam, was dictated by the geometry and space limitations of the mass spectrometer.

The entire Knudsen cell assembly is supported by a baseplate attached to the flange that seals the Knudsen cell assembly into its vacuum housing. The Knudsen cell itself is supported by a tantalum pedestal held on 0.060-inch- (0.15-cm-) diameter zirconia rods which fit into a boron nitride block attached to the baseplate. This cell support arrangement has proved to be mechanically stable during heating and cooling of the cell.

Immediately around the Knudsen cell and concentric with it are located two filaments used to heat the cell. One filament is located near the top and the other near the bottom of the cell. Each filament actually consists of two semicircles of 0.004- by 0.030-inch (0.01- by 0.076-cm) tungsten ribbon electrically in parallel. The semicircles are held in place by two 0.125-inch- (0.318-cm-) diameter slotted tungsten rods which also serve as the electrical leads. These rods are mechanically attached to the baseplate but are electrically and thermally insulated from it. Each filament is heated by a 0.5-kilovolt-

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ampere alternating-current power source. The power in each filament can be adjusted independently to eliminate any vertical temperature gradients in the Knudsen cell. The maximum cell temperature attainable by radiation alone is approximately 1500 K. With constant power to the filaments, the temperature varied by only about ±3 K, the precision of the optical pyrometer used. To attain temperatures greater than 1500 K the cell is heated by electron bombardment. In this mode the cell is put at a high potential relative to the filaments. The power supply used can provide a cell potential of from 200 to 1000 volts and a total emission current as large as 5 amperes. Temperature control is achieved by automatic regulation of power. Typical regulation of temperature at 2200 K is ±5 K. With this heating arrangement a tungsten cell has been heated to 2700 K for extended periods of time. Only about half the available power was required.

The Knudsen cell and heating filaments are surrounded on the top and sides by four concentric cans which form the upper heat shields. All shields are formed from 0.005-inch (0.013-cm) tantalum. A 0.062-inch- (0.157-cm-) thick boron nitride ring facilitates fastening the upper shields to the baseplate while still providing electrical and thermal isolation. The lower shields are supported from the baseplate by zirconia rods and spacers. Holes in the upper shields provide a view of the blackbody holes in the cell and a passage for the effusing molecular beam, respectively.

The baseplate holding the entire Knudsen cell assembly is attached to the end flange with a hinge permitting a horizontal arc movement of the plate and assembly. Remote control of the motion is possible by the operation of a micrometer screw outside the vacuum chamber. This mechanism provides a convenient means of optimizing alinement of the cell to obtain maximum beam transmission into the ion source.

Between the Knudsen cell assembly and the entrance to the ion source is a solid copper plate which serves to isolate the Knudsen cell region from the ion source. This plate has a single opening in line with the effusion orifice and ion source entrance slit. This opening can be closed optically by a slit shutter whose movement is controlled by a micrometer screw external to the vacuum chamber. The shutter does not provide a gas-tight seal between the Knudsen cell vacuum chamber and the ion source. The tantalum shutter slit may be used to block the molecular beam, to allow optimum passage of the beam, or to scan the beam to study its profile.

The Knudsen cell vacuum chamber is pumped with a 100-liter-per-second oil diffusion pump and liquid-nitrogen cold trap. When the Knudsen cell is at room temperature, the pressure in this chamber is maintained in the high 10^{-8}-torr range as read by a Bayard-Alpert type ionization gage located at the Knudsen cell chamber. When samples yielding only condensible molecules are being heated, the pressure can be maintained in the 10^{-7}-torr range. The Knudsen cell chamber and an internal copper baffle which partially surrounds the cell assembly are water-cooled.

Ion Source

The ion source is of the electron impact type. Upon entering the ion source the molecular beam passes through the collimating slit and between a pair of deflector plates into the ionization chamber proper. The collimating slit is 0.025 inch (0.064 cm) wide and floating with respect to ground. The deflector plates are separated by about 0.062 inch (0.157 cm), and in this study both were maintained at the ionization chamber potential of 8 kilovolts. However, one plate may be grounded to remove any ionic species originating in the Knudsen cell region.

The ionization chamber itself is set off by a 0.015-inch (0.038-cm) entrance slit and a 0.025-inch (0.064-cm) exit slit. A shielded rhenium filament 0.007 inch (0.018 cm) in diameter is located just outside the ionization chamber. Electrons pass from the filament through alined openings in the chamber to the gold anode on the opposite side of the chamber in such a way that they intersect the molecular beam at right angles. A permanent magnet is used to focus the electron beam. The filament can be held at a potential of -3 to -53, -70, or -150 volts with respect to the chamber. The anode is held at 0 to 70 or 150 volts relative to the chamber. Filament emission current is automatically regulated at any selected value in the range 0 to 200 microamperes. Within the ionization chamber are a pair of repeller plates whose potential can be independently varied from 0 to 200 volts relative to the chamber. In practice, the repellers are usually held at a potential of less than 10 volts.

The focus slit located after the ion chamber exit is made in two parts so that a potential difference can be placed across the slit. The potential is used to direct the ion beam through the source slit and into the analyzer of the mass spectrometer. The focus slit is 0.025 inch (0.064 cm) wide and is maintained at a potential between 0 and -200 volts with respect to the ion chamber. The width of the source slit is adjustable over the range 0 to 0.020 inch (0 to 0.050 cm) by a micrometer screw located outside the ion source vacuum chamber. This slit is the last in the ion source and is maintained at ground potential.

The ion source region is pumped by a 100-liter-per-second oil diffusion pump and liquid-nitrogen trap. Pressure in this region is usually maintained in the low 10^{-7}-torr range as read by a Bayard-Alpert ion gage located at the ion source vacuum housing. An isolation valve separates the ion source from the analyzer. By differential pumping, a differential pressure of at least a factor of 10 can be maintained between the Knudsen cell vacuum chamber and the ion source vacuum chamber. Similarly, a factor of 100 in pressure can be maintained between the ion source vacuum chamber and the mass analyzer under operating conditions.

Mass Analyzer and Detector

The analyzer consists of tandem electrostatic and magnetic sectors as shown in figure 1. The beam of ions of mixed mass and velocity emerging from the source slit travels down the field free-drift tube into the electric sector. After traversing the electric sector, where velocity focusing occurs, the ion beam enters the magnetic sector. Here it is separated into a series of beams composed of different mass components.

Each individual mass beam is brought into focus at the ion collector by varying the magnetic field. The beam passes through the collector slit, located at the maximum radius allowed by the magnet, and encounters the detector. Either a Faraday cup collector or an electron multiplier can be selected.

The electron multiplier used in this study is of the "Venetian blind" type with 17 copper-beryllium (Cu-Be) dynodes. The potential of each dynode is adjustable between 128 and 252 volts, thus providing a multiplier of variable gain. Output current from the Faraday collector or electron multiplier is measured with a vibrating reed electrometer and recorded on a strip-chart recorder. With this measuring system, the possible dynamic range is 3×10^{11}.

The vacuum system of the analyzer is pumped by a 600-liter-per-second oil diffusion pump and liquid-nitrogen trap. Pressure in the analyzer is maintained in the 10^{-8}-torr range as read by a Bayard-Alpert ion gage located at the electric sector.

The widths of the source slit and collector slit are adjustable to produce a desired resolution. Resolution can be varied from 700 to 2000 (10 percent valley definition) without substantial loss in sensitivity.

EXPERIMENTAL

Knudsen Cell

The sintered tungsten Knudsen cell used in this investigation was 1.0 inch (2.54 cm) high and 0.75 inch (1.91 cm) in diameter with a wall thickness of 0.125 inch (0.318 cm). The knife-edged orifice had an area of 1.27×10^{-2} square centimeter. The 0.125-inch- (0.318-cm-) thick step-type lid fit snugly into the crucible body. Three blackbody holes of 0.039 inch (0.099 cm) diameter were located to the rear of the cell in a vertical line, one near the top, one near the middle, and one near the bottom. A special design of the holes gave a ratio of hole to inside surface area of at least 50. The ratio of sample surface area to orifice area was greater than 100.

Temperature Measurements

Temperatures were measured with a calibrated disappearing-filament-type optical pyrometer by sighting through a flat glass window into the blackbody holes. Any vertical gradients in the cell were minimized by appropriate adjustments of the upper and lower filament power so that the cell blackbody holes indicated the same temperature within the precision of the pyrometer. Experimentally determined window corrections were applied to all temperature readings. The window is protected from subliming vapors by a magnetically actuated shutter.

Preparation of Sample

The TiN sample was prepared by Jack E. Tetzlaff of this laboratory by passing high-purity ammonia (NH_3) at 1.5-atmosphere pressure over electronic grade titanium hydride placed in a TiN boat. The titanium hydride had been obtained from Metal Hydrides, Inc. with a reported maximum impurity analysis of 0.2-weight-percent oxygen (O_2) and 0.05 weight percent each of cobalt (Co), magnesium (Mg), aluminum (Al), and zirconium (Zr). Throughout the preparation, the temperature of the titanium hydride was maintained at 1570 K. The sample was subsequently heated under several atmospheres of high-purity nitrogen at 1870 K. The results of titanium and nitrogen analyses indicated that the sample composition was $TiN_{0.98}$. The analysis was carried out by a newly developed method to be published by Warren H. Philipp and Jack E. Tetzlaff of Lewis.

Procedure

A 2.13-gram sample of powdered $TiN_{0.98}$ was placed into the Knudsen cell and heated for extended periods of time at temperatures of 1600 to 2200 K. The background pressures in the Knudsen cell region rose from the 10^{-7}-torr range at 1600 K to the high 10^{-5}-torr range at 2300 K during these preliminary heatings.

Ion intensity measurements were made with ionizing electrons of 30 electron volts and a emission current of 100 microamperes. The ionic species were identified in the usual manner by their ratios of mass to charge and isotopic abundance distributions. Proof as to which species were originating from the Knudsen cell was established by shutter profile measurements. The measured ion currents for each species originating from the Knudsen cell correspond to the difference between the signal measured with the shutter in the open position and the shutter in the closed position. For a series of
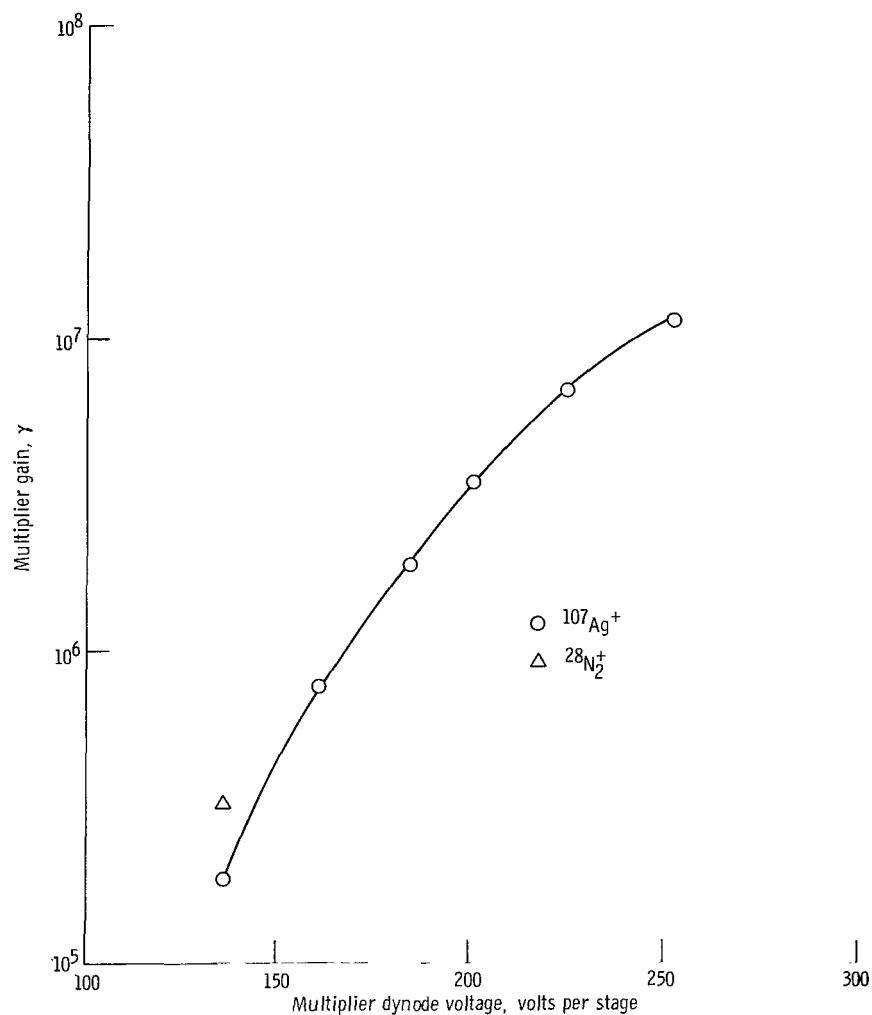
Figure 5. - Absolute multiplier gain as function of multiplier dynode voltage.

measurements, the focusing controls of the instrument were adjusted to yield a maximum ion current for one of the condensible species effusing from the cell. In the early stages of the vaporization at temperatures above 1650 K, measurable intensities for N_2^+ and Ti^+ were recorded. The ratio of $^{28}N_2^+$ to $^{48}Ti^+$ was generally between 10 and 100. At temperatures above 1800 K, the TiO^+ ion spectrum observed had an intensity ratio of $^{64}TiO^+$ to $^{48}Ti^+$ approximately equal to 0.01. The Ti^+ and TiO^+ spectra agreed with the natural isotopic abundance ratios within a few percent. Chemical and X-ray analyses of the un-vaporized sample after several heatings showed that the TiN was vaporizing incongruently and the solid was becoming richer in titanium. By visual observation it was apparent that there had been no reaction between the TiN sample and the tungsten cell.

When the sample stoichiometry was approximately $TiN_{0.79}$, a 0.80-gram sample of this material and a small amount of silver (Ag) for calibration purposes were placed into

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the Knudsen cell. The intensities of the $^{107}Ag^+$ and $^{109}Ag^+$ ions were measured at several temperatures between 1200 and 1400 K. The relative intensities of the $^{107}Ag^+$ and $^{109}Ag^+$ ions were in agreement with the natural isotopic abundance ratio within a few percent. The Knudsen cell was then taken to higher temperatures in an attempt to observe the TiN^+ ion.

At the high temperatures, the large ion currents of Ti^+ and N_2^+ were collected by the Faraday cup and recorded directly or were obtained from the electron multiplier operated at reduced gain. The absolute multiplier gain γ was measured for N_2^+ and Ti^+ as 3.25×10^5 and 1.88×10^5, respectively, at a multiplier dynode potential of 136 volts per stage. The relative gain as a function of multiplier voltage was measured for Ag^+ in a separate experiment and was found to be in excellent agreement with that measured for Ti^+. The relative gain for N_2^+ was taken to be the same as that for Ag^+ and Ti^+. It was assumed that the absolute gains for Ag^+, Ti^+, and TiN^+ were identical (ref. 7). In figure 5 the multiplier gain is given as a function of multiplier dynode voltage.

EXPERIMENTAL RESULTS

The TiN^+ ion was positively identified at 2279, 2360, and 2456 K. Ion intensities for Ti^+, N_2^+, TiN^+, TiO^+, and Ni^+ were measured at each temperature. At 2279 K the relative ion intensities of $^{48}Ti^+$, $^{28}N_2^+$, $^{60}TiN^+$, and $^{64}TiO^+$ were 1.00, 0.66, 1.3×10^{-6} and 1.4×10^{-2}. Because of the presence of a much larger TiO^+ intensity, the TiN^+ isotopic distribution could be measured only at mass numbers 60 and 61. An additional point of concern in this case was the presence of the ions $^{60}Ni^+$ and $^{61}Ni^+$ appearing as ion species whose precursors originated in the Knudsen cell. The resolution of the instrument during this experiment was measured as approximately 1400. This was sufficient to separate the organic background peaks at masses 60 and 61 from any inorganic species. This resolution was also adequate to provide a workable separation between the $^{60}Ni^+/^{60}TiN^+$ and $^{61}Ni^+/^{61}TiN^+$. An example of a typical scan in this region of the spectrum is shown in figure 6. At 2279 K, the ratio of $^{60}TiN^+$ to $^{60}Ni^+$ was 1.6. At the highest temperature of this investigation (2456 K), the ratio of $^{60}TiN^+$ to $^{60}Ni^+$ was approximately 1.8.

The relative intensities of $^{60}TiN^+$ and $^{61}TiN^+$ agreed reasonably well with the natural isotopic abundance of ^{46}Ti and ^{47}Ti. The ion intensities of the various species appeared to be fairly constant over the short period of time during which the measurements were made.

Because in all cases the TiN^+ ion was a minor species of minimal intensity, no appearance potential could be measured for this species. However, the ions at masses 60 and 61 exhibited a normal shutter effect. With the combination of elements present
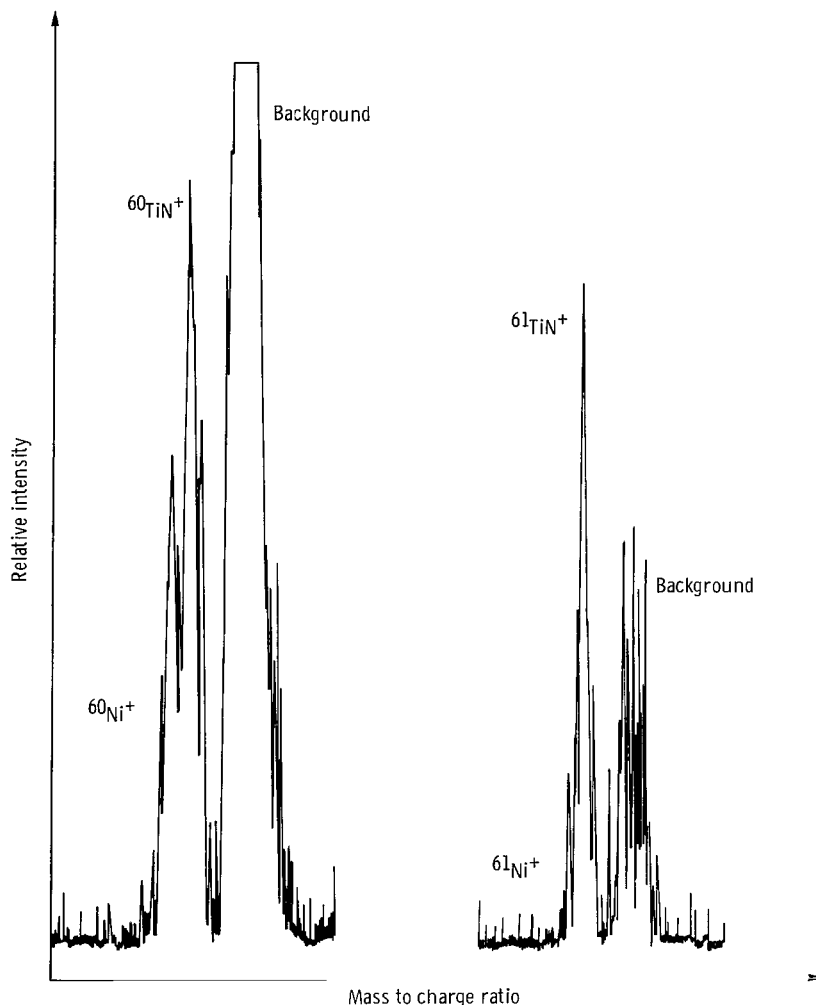
Figure 6. - Typical spectrum in region of mass to charge ratios 60 and 61 showing resolution of Ni^+, TiN^+, and organic background ions.

in the system along with a consideration of the resolving power of the instrument, the identification of the resolved masses 60 and 61 as TiN^+ is positive. Our experimentally measured molecular weight for $^{60}TiN^+$ agreed within 0.002 mass units with the theoretical value.

In this investigation the ion beam was focused on either the $^{107}Ag^+$ or $^{48}Ti^+$ ion. For the measurements of N_2^+ and TiN^+, the same focus settings were used as for $^{48}Ti^+$. The shutter effect measured for N_2^+ was between 11 and 22 percent of the total N_2^+ ion current, while the shutter effects for Ti^+, TiN, and TiO^+ were essentially 100 percent. The N_2^+ shutter effect was not higher because, under the conditions in the Knudsen cell region, the pumping speeds prevented its complete instantaneous removal. However, we believe that the shutter-corrected intensities for N_2^+ are a reliable indication of the

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amount of nitrogen gas effusing from the cell.

The metallic ions of vanadium, chromium, manganese, iron, and nickel (V^+, Cr^+, Mn^+, Fe^+, and Ni^+) were detected at high temperatures. These metal ions were 100 percent shutterable, and thus are believed to derive from the Knudsen cell. In all cases, the intensity level of these ions was relatively low. Analysis of the titanium nitride after the experiment gave a composition of $TiN_{0.78}$.

During the silver calibrations the Ag_2^+ ion was identified, and its intensity was measured at 1305 and 1367 K.

CALCULATIONS AND DISCUSSION

The measured ion currents I_i^+ for Ti^+, N_2^+, and TiN^+ were converted to the corresponding partial pressures P_i by using the standard relation $P_i = kI_i^+ T/\sigma_i \gamma_i n_i$ where k is the sensitivity constant, σ_i the relative ionization cross section, γ_i the relative multiplier gain, and n_i the fractional isotopic abundance of the species i. The sensitivity constant was determined by means of the silver calibration. The values for the vapor pressure of silver as a function of temperature were taken from the compilation of Hultgren, et al., (ref. 8).

The dissociation energy D_0^0 of Ag_2 was calculated from measured ion intensities and found to be 35.2±3.0 kilocalories mole^{-1} (147.3±12 kJ mole^{-1}). This value compares favorably with the literature value (ref. 9) of 37.6±2.2 kilocalories mole^{-1} (157.3±9.2 kJ mole^{-1}).

The relative maximum ionization cross sections were taken from Mann (ref. 10). The relative cross section of N_2 was obtained by multiplying Mann's atomic cross section for nitrogen by the experimentally determined factor $\sigma_{N_2}/\sigma_N = 1.93$ (ref. 11). The relative cross section of TiN was estimated by multiplying the sum of Mann's atomic cross sections with an empirical factor of 0.7 (ref. 12). The relative ionization cross sections used were 5.44 for Ag, 5.97 for Ti, 2.66 for N_2, and 5.14 for TiN. It was assumed that all of the ionization efficiency curves had their maximums at or near 30 electron volts. The partial pressures of Ti, N_2, and TiN were calculated, and the values are listed in table I and illustrated in figure 7.

Several points must be discussed in relation to the accuracy of the experimental measurements. Dreger and Margrave (ref. 13) carried out Langmuir vaporization experiments on a titanium nitride sample and obtained a heat of decomposition of 143.1 kilocalories mole^{-1} (598.7 kJ mole^{-1}) using an evaporation coefficient of 0.155. McClaine and Coppel (ref. 14) have measured the nitrogen and titanium equilibrium pressure over titanium nitrides of various stoichiometries and originally concluded that the vaporization coefficient for N_2 may be in the range of 0.01 to 0.001. However, the presence of rather

TABLE I. - PARTIAL PRESSURES AND THIRD-LAW ENTHALPY

VALUES FOR REACTION TiN(g) = Ti(g) + 0.5 N_2(g)

Temperature, K	Ti		N_2		TiN	
	Partial pressure, P					
	atm	N/m^2	atm	N/m^2	atm	N/m^2
1730	$2.42{\times}10^{-7}$	$2.44{\times}10^{-2}$	$1.49{\times}10^{-7}$	$1.50{\times}10^{-2}$	---------	---------
2102	$7.46{\times}10^{-5}$	$7.53{\times}10^{0}$	$3.83{\times}10^{-5}$	$3.87{\times}10^{0}$	---------	---------
2279	$5.04{\times}10^{-4}$	$5.09{\times}10^{1}$	$4.77{\times}10^{-4}$	$4.82{\times}10^{1}$	$6.32{\times}10^{-9}$	$6.29{\times}10^{-4}$
2360	$8.07{\times}10^{-4}$	$8.15{\times}10^{1}$	$5.92{\times}10^{-4}$	$5.98{\times}10^{1}$	$1.07{\times}10^{-8}$	$1.08{\times}10^{-3}$
2456	$1.89{\times}10^{-3}$	$1.91{\times}10^{2}$	$1.04{\times}10^{-3}$	$1.05{\times}10^{2}$	$5.23{\times}10^{-8}$	$5.28{\times}10^{-3}$

Temperature, K	Equilibrium constant, $\log_{10} K_p$	Change of Gibbs' free-energy functions, $-\Delta\left[(G_T^o - H_{298}^o)/T\right]$		Third-law enthalpy, ΔH_{298}^o	
		cal deg^{-1} mole^{-1}	J deg^{-1} mole^{-1}	kcal mole^{-1}	kJ mole^{-1}
1730	-----	-----	-----	-----	------
2102	-----	-----	-----	-----	------
2279	3.241	13.81	57.78	-2.33	-9.75
2360	3.264	13.83	57.86	-2.60	-10.88
2456	3.066	13.86	57.99	-.42	-1.76
			Average	-1.78	-7.45

substantial errors in the measurement of temperature for their experiments, reported in a subsequent publication (ref. 15), would seem to invalidate most of the conclusions drawn. The existence of a vaporization coefficient less than 1 has pertinence on the work of Dreger and Margrave, but it need not concern us here since the only reaction being studied is a gas-phase reaction. A vaporization coefficient of approximately 0.1 would also not interfere in the investigation of solid-gas equilibria in this case since the ratio of sample surface area to orifice area was greater than 100.

Because of the necessarily high pressures of Ti and N_2 in the Knudsen cell, the requirement for effusive flow (that the ratio of the mean free path of the molecules to the orifice diameter be greater than 1) is not met in this investigation. Nevertheless, in practice, ratios of 1 are acceptable (ref. 16), and satisfactory results have been obtained in other investigations (refs. 17 to 19) with ratios much smaller than 1. Small deviations from effusive flow have little effect on the equilibrium constants calculated for the reaction under consideration.
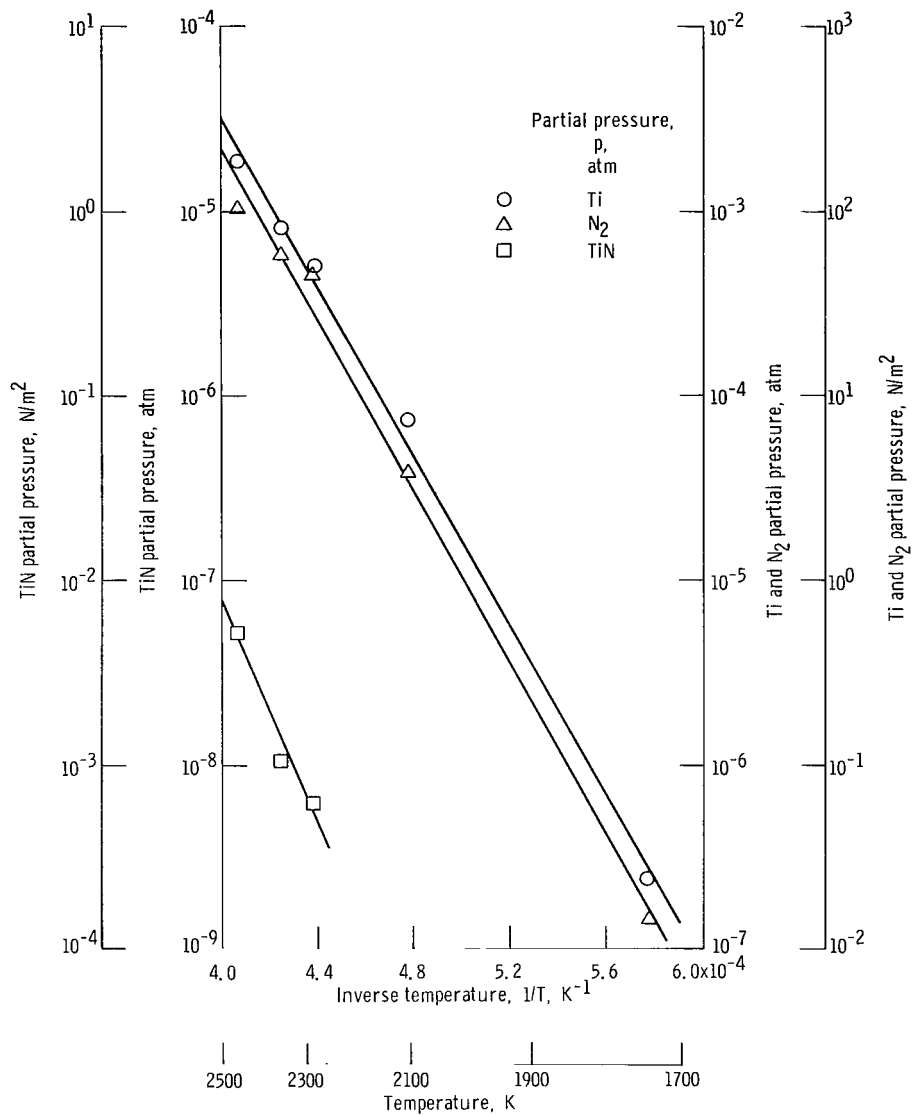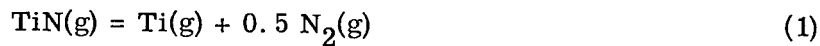
Figure 7. – Partial pressures of Ti, N_2, and TiN as function of reciprocal temperature over solid $TiN_{0.78}$.

From the partial pressures of the Ti, N_2, and TiN, the third-law enthalpy ΔH^o_{298} for the reaction

$$TiN(g) = Ti(g) + 0.5 \ N_2(g) \tag{1}$$

was calculated according to the relation

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$$\Delta H^O_{298} = -RT \ln K_p - T \Delta \left[\frac{\left(G^O_T - H^O_{298} \right)}{T} \right] \tag{2}$$

where

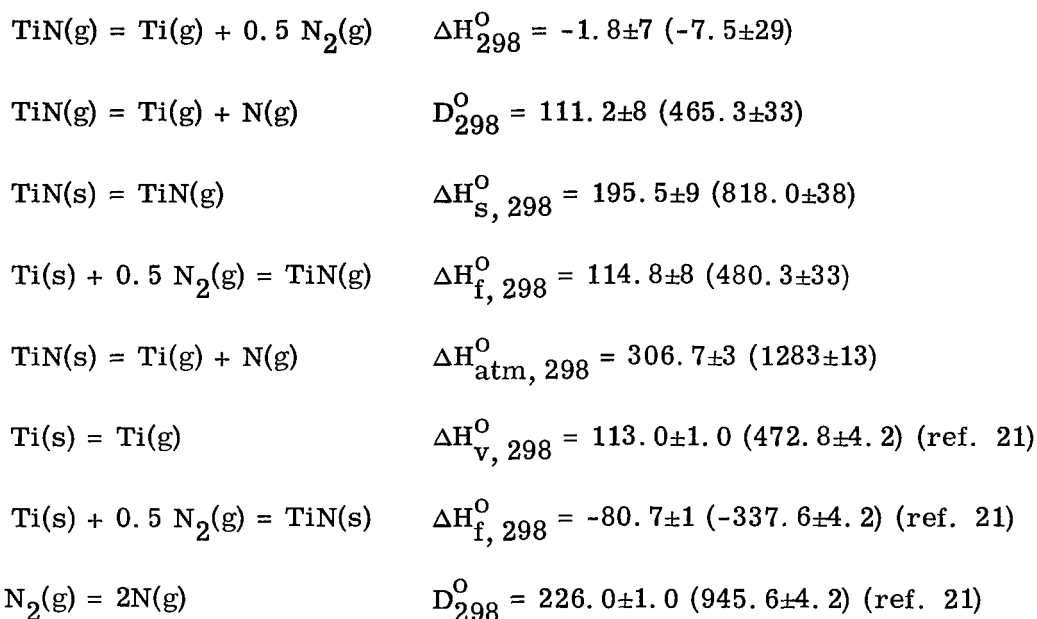$$K_p = \frac{\left(P_{Ti} \right)\left(P_{N_2} \right)^{1/2}}{\left(P_{TiN} \right)} \tag{3}$$

is the equilibrium constant and $\Delta\left[\left(G^O_T - H^O_{298}\right)/T\right]$ is the change of the Gibbs free-energy functions for the reaction. The results of these calculations are also presented in table I. The values of the free-energy functions for Ti(g) and N_2(g) were taken from the JANAF tables (ref. 20). The free-energy functions for TiN(g) were calculated with the aid of Bonnie J. McBride on the basis of the molecular parameters for the TiN molecule estimated by Carlson, et al., (ref. 4). The ground state of TiN was taken as $^2\Sigma^+$. An internuclear distance of 1.55 Å was used along with the fundamental vibrational frequency of 1080 centimeters^{-1} and an anharmonicity constant of 6 centimeters^{-1}. The $-\left(G^O_T - H^O_{298}\right)/T$ values in calories mole^{-1} degree^{-1} (J mole^{-1} degree^{-1}) calculated for TiN(g) were 62.43 (261.21) at 2200 K, 62.76 (262.59) at 2300 K, 63.08 (263.93) at 2400 K, and 63.39 (265.22) at 2500 K. The average value for the heat of reaction (1) was calculated to be -1.8 kilocalories mole^{-1} (-7.5 kJ mole^{-1}). Taking into account the estimated errors in the intensities, cross sections, multiplier gains, temperature measurements, and free-energy functions, the value of ±7 kilocalories (±29 kJ) was obtained for the estimated error. This value of ΔH^O_{298} = 1.8±7 kilocalories mole^{-1} (-7.5±29 kJ mole^{-1}) was then combined with the known dissociation energy of N_2 (ref. 20) (D^O_{298} = 226.0±1.0 kcal mole^{-1} or 945.6±4.2 kJ mole^{-1}) to obtain the dissociation of gaseous TiN as D^O_{298} = 111.2±8 kilocalories mole^{-1} (465.3±33 kJ mole^{-1}) or D^O_0 = 110.0±8 kilocalories mole^{-1} (460.2±33 kJ mole^{-1}). A comparison of our value with the estimated values of D^O_0 = 125 kilocalories mole^{-1} (523 kJ mole^{-1}) and D^O_{298} = 123±10 kilocalories mole^{-1} (515±42 kJ mole^{-1}) suggests that the basis for these estimates is reasonable in that the values agree within their uncertainties.

The heat of formation $\Delta H^O_{f, 298}$ of TiN(g) was obtained as 114.8±8 kilocalories mole^{-1} (480.3±33 kJ mole^{-1}) from the heat of sublimation of titanium (ref. 20), $\Delta H^O_{v, 298}$ = 113.0±1.0 kilocalories mole^{-1} (472.8±4.2 kJ mole^{-1}), and the enthalpy of reaction (ref. 1). This value can be compared with the estimated value (ref. 5) of 102±12 kilocalories mole^{-1} (427±50 kJ mole^{-1}). The heat of sublimation of TiN, $\Delta H^O_{s, 298}$ = 195.5±9 kilocalories mole^{-1} (818.0±38 kJ mole^{-1}) has been calculated on the basis of the standard heat of formation for stoichiometric TiN(s) of -80.7±1 kilocalories mole^{-1}

$(-337.6\pm4.2 \text{ kJ mole}^{-1})$ (ref. 20). This value can be compared with the estimated value (ref. 5) of 183 ± 12 kilocalories mole^{-1} $(766\pm50 \text{ kJ mole}^{-1})$.

The heat of atomization of TiN(s), $\Delta H^O_{atm, 298}$, was calculated as 306.7 ± 3 kilocalories mole^{-1} $(1283\pm13 \text{ kJ mole}^{-1})$. Thus, the α-parameter (ref. 6) $\left(\alpha = 0.5 \ \Delta H^O_{atm, 298}/D^O_{298}\right)$ is equal to 1.38. This value compares with the values of α for other gaseous nitrides (ref. 5) of 1.28 for ZrN, 1.24 for ThN, and 1.20 for UN.

The heats of reactions for the Ti-N system in kilocalories mole^{-1} (kJ mole^{-1}) are summarized as follows:

$$\text{TiN(g)} = \text{Ti(g)} + 0.5 \ \text{N}_2\text{(g)} \qquad \Delta H^O_{298} = -1.8\pm7 \ (-7.5\pm29)$$

$$\text{TiN(g)} = \text{Ti(g)} + \text{N(g)} \qquad D^O_{298} = 111.2\pm8 \ (465.3\pm33)$$

$$\text{TiN(s)} = \text{TiN(g)} \qquad \Delta H^O_{s, 298} = 195.5\pm9 \ (818.0\pm38)$$

$$\text{Ti(s)} + 0.5 \ \text{N}_2\text{(g)} = \text{TiN(g)} \qquad \Delta H^O_{f, 298} = 114.8\pm8 \ (480.3\pm33)$$

$$\text{TiN(s)} = \text{Ti(g)} + \text{N(g)} \qquad \Delta H^O_{atm, 298} = 306.7\pm3 \ (1283\pm13)$$

$$\text{Ti(s)} = \text{Ti(g)} \qquad \Delta H^O_{v, 298} = 113.0\pm1.0 \ (472.8\pm4.2) \ (\text{ref. 21})$$

$$\text{Ti(s)} + 0.5 \ \text{N}_2\text{(g)} = \text{TiN(s)} \qquad \Delta H^O_{f, 298} = -80.7\pm1 \ (-337.6\pm4.2) \ (\text{ref. 21})$$

$$\text{N}_2\text{(g)} = 2\text{N(g)} \qquad D^O_{298} = 226.0\pm1.0 \ (945.6\pm4.2) \ (\text{ref. 21})$$

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 22, 1968,
129-03-15-02-22.

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